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(54) Title: FUEL ADDITIVE COMPOSITIONS CONTAINING POLYALKYPHOXYAMINOALKANES AND			
(57) Abstract <p>A fuel additive composition comprising: (a) a polyalkylphenoxyaminoalkane having formula (I) or a fuel soluble salt thereof, wherein R is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000; R₁ and R₂ are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and A is amino, N-alkyl amino having 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms; and (b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel fuel range. The fuel additive compositions of this invention are useful as fuel additives for the prevention and control of engine deposits.</p>			
(I)			

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-1-

01
02 FUEL ADDITIVE COMPOSITIONS
03 CONTAINING POLYALKYLPHENOXYAMINOALKANES
04 AND POLY(OXYALKYLENE) AMINES

05

06 BACKGROUND OF THE INVENTION

07

08 Field of the Invention

09

10 This invention relates to fuel additive compositions
11 containing polyalkylphenoxyaminoalkanes and
12 poly(oxyalkylene) amines. In a further aspect,
13 this invention relates to the use of these additive
14 compositions in fuel compositions to prevent and control
15 engine deposits.

16

17 Description of the Related Art

18

19 It is well known that automobile engines tend to form
20 deposits on the surface of engine components, such as
21 carburetor ports, throttle bodies, fuel injectors, intake
22 ports and intake valves, due to the oxidation and
23 polymerization of hydrocarbon fuel. These deposits, even
24 when present in relatively minor amounts, often cause
25 noticeable driveability problems, such as stalling and poor
26 acceleration. Moreover, engine deposits can significantly
27 increase an automobile's fuel consumption and production of
28 exhaust pollutants. Therefore, the development of effective
29 fuel detergents or "deposit control" additives to prevent or
30 control such deposits is of considerable importance and
31 numerous such materials are known in the art.

32

33 For example, aliphatic hydrocarbon-substituted phenols are
34 known to reduce engine deposits when used in fuel

-2-

01 compositions. U.S. Patent No. 3,849,085, issued
02 November 19, 1974 to Kreuz et al., discloses a motor fuel
03 composition comprising a mixture of hydrocarbons in the
04 gasoline boiling range containing about 0.01 to 0.25 volume
05 percent of a high molecular weight aliphatic
06 hydrocarbon-substituted phenol in which the aliphatic
07 hydrocarbon radical has an average molecular weight in the
08 range of about 500 to 3,500. This patent teaches that
09 gasoline compositions containing minor amounts of an
10 aliphatic hydrocarbon-substituted phenol not only prevent or
11 inhibit the formation of intake valve and port deposits in a
12 gasoline engine, but also enhance the performance of the
13 fuel composition in engines designed to operate at higher
14 operating temperatures with a minimum of decomposition and
15 deposit formation in the manifold of the engine.

16

17 U.S. Patent No. 4,259,086, issued March 31, 1981 to
18 Machleider et al., discloses a detergent additive for fuels
19 and lubricating oils which comprises the reaction product of
20 an aliphatic hydrocarbon-substituted phenol, epichlorohydrin
21 and a primary or secondary monoamine or polyamine. In
22 addition, U.S. Patent No. 4,048,081, issued September 13,
23 1977 to Machleider et al., discloses a detergent additive for
24 gasoline which is the reaction product of a polyisobutene
25 phenol with epichlorohydrin, followed by amination with
26 ethylene diamine or other polyamine.

27

28 Similarly, U.S. Patent No. 4,134,846, issued January 16,
29 1979 to Machleider et al., discloses a fuel additive
30 composition comprising a mixture of (1) the reaction product
31 of an aliphatic hydrocarbon-substituted phenol,
32 epichlorohydrin and a primary or secondary mono- or
33 polyamine, and (2) a polyalkylene phenol. This patent
34 teaches that such compositions show excellent carburetor,

-3-

01 induction system and combustion chamber detergency and, in
02 addition, provide effective rust inhibition when used in
03 hydrocarbon fuels at low concentrations.

04

05 Amino phenols are also known to function as
06 detergents/dispersants, antioxidants and anti-corrosion
07 agents when used in fuel compositions. U.S. Patent
08 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for
09 example, discloses amino phenols having at least one
10 substantially saturated hydrocarbon-based substituent of at
11 least 30 carbon atoms. The amino phenols of this patent are
12 taught to impart useful and desirable properties to
13 oil-based lubricants and normally liquid fuels.

14

15 In addition, polybutylamines have been taught to be useful
16 for preventing deposits in the intake system of internal
17 combustion engines. For example, U.S. Patent No. 4,832,702,
18 issued May 23, 1989 to Kummer et al., discloses fuel and
19 lubricant compositions containing polybutyl or
20 polyisobutylamine additives prepared by hydroformulating a
21 polybutene or polyisobutene and then subjecting the
22 resulting oxo product to a Mannich reaction or amination
23 under hydrogenating conditions.

24

25 Polyether amine fuel additives are also well known in the
26 art for the prevention and control of engine deposits.
27 These polyether additives have a polyoxyalkylene "backbone",
28 i.e., the polyether portion of the molecule consists of
29 repeating oxyalkylene units. U.S. Patent No. 4,191,537,
30 issued March 4, 1980 to Lewis et al., for example, discloses
31 a fuel composition comprising a major portion of
32 hydrocarbons boiling in the gasoline range and from 30 to
33 2,000 ppm of a hydrocarbyl polyoxyalkylene aminocarbamate
34 having a molecular weight from about 600 to 10,000, and at

-4-

01 least one basic nitrogen atom. The hydrocarbyl
02 polyoxyalkylene moiety is composed of oxyalkylene units
03 having from 2 to 5 carbon atoms in each oxyalkylene unit.
04 These fuel compositions are taught to maintain the
05 cleanliness of intake systems without contributing to
06 combustion chamber deposits.

07
08 Aromatic compounds containing a poly(oxyalkylene) moiety are
09 also known in the art. For example, the above-mentioned U.S.
10 Patent No. 4,191,537, discloses alkylphenyl
11 poly(oxyalkylene) polymers which are useful as intermediates
12 in the preparation of alkylphenyl poly(oxyalkylene)
13 aminocarbamates.

14
15 Similarly, U.S. Patent No. 4,881,945, issued November 21,
16 1989 to Buckley, discloses a fuel composition comprising a
17 hydrocarbon boiling in the gasoline or diesel range and from
18 about 30 to about 5,000 parts per million of a fuel soluble
19 alkylphenyl polyoxyalkylene aminocarbamate having at least
20 one basic nitrogen and an average molecular weight of about
21 800 to 6,000 and wherein the alkyl group contains at least
22 40 carbon atoms.

23
24 U.S. Patent No. 5,112,364, issued May 12, 1992 to
25 Rath et al., discloses gasoline-engine fuels which contain
26 small amounts of a polyetheramine and/or a polyetheramine
27 derivative, wherein the polyetheramine is prepared by
28 reductive amination of a phenol-initiated or alkylphenol-
29 initiated polyether alcohol with ammonia or a primary amine.

30
31 U.S. Patent No. 4,247,301, issued January 27, 1981 to
32 Honnen, discloses hydrocarbyl-substituted poly(oxyalkylene)
33 polyamines, wherein the hydrocarbyl group contains from 1 to
34 30 carbon atoms and the polyamine moiety contains from 2 to

01 12 amine nitrogen atoms and from 2 to 40 carbon atoms. This
02 patent teaches that the additives may be prepared by the
03 reaction of a suitable hydrocarbyl-terminated polyether
04 alcohol with a halogenating agent, such as HCl or thionyl
05 chloride, to form a polyether chloride, followed by reaction
06 of the polyether chloride with a polyamine to form the
07 desired poly(oxyalkylene) polyamine. This patent also
08 teaches at Example 6 that the polyether chloride may be
09 reacted with ammonia or dimethylamine to form the
10 corresponding polyether amine or polyether dimethylamine.

11
12 European Patent Application Publication No. 310,875,
13 published April 12, 1989 discloses fuels for spark ignition
14 engines containing a polyetheramine additive prepared by
15 first propoxylating and/or butoxylating an alkanol or
16 primary or secondary alkylmonoamine and then aminating the
17 resulting polyether with ammonia or a primary aliphatic
18 amine.

19
20 French Patent No. 2,105,539, published April 28, 1972,
21 discloses carburetor detergent additives which are
22 phenoxypropylamines which may be substituted with up to five
23 hydrocarbon radicals of 1 to 30 carbon atoms on the aromatic
24 ring. This patent also discloses additives obtained by
25 reacting such phenoxypropylamines with alkylphosphoric
26 acids.

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-6-

01 SUMMARY OF THE INVENTION

02

03 It has not been discovered that the combination of certain
04 polyalkylphenoxyaminoalkanes with poly(oxyalkylene) amines
05 provides excellent control of engine deposits, especially
06 intake valve deposits, when employed as fuel additives in
07 fuel compositions.

08

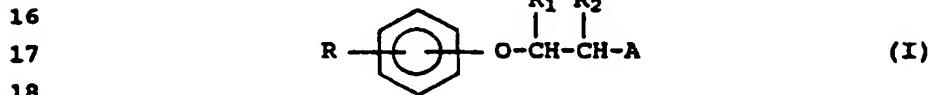
09 Accordingly, the present invention provides a novel fuel
10 additive composition comprising:

11

12 (a) A polyalkylphenoxyaminoalkane compound having the
13 following formula or a fuel soluble salt thereof:

14

15



17

18 wherein R is a polyalkyl group having an average
19 molecular weight in the range of about 600 to 5,000;

20

21 R₁ and R₂ are independently hydrogen or lower alkyl
22 having 1 to 6 carbon atoms; and

23

24 A is amino, N-alkyl amino having about 1 to about
25 20 carbon atoms in the alkyl group, N,N-dialkyl amino
26 having about 1 to about 20 carbon atoms in each alkyl
27 group, or a polyamine moiety having about 2 to about
28 12 amine nitrogen atoms and about 2 to about 40 carbon
29 atoms; and

30

31 (b) a poly(oxyalkylene) amine having at least one basic
32 nitrogen atom and a sufficient number of oxyalkylene

-7-

01 units to render the poly(oxyalkylene) amine soluble in
02 hydrocarbons boiling in the gasoline or diesel fuel
03 range.

04

05 The present invention further provides a fuel
06 composition comprising a major amount of hydrocarbons
07 boiling in the gasoline or diesel range and an
08 effective deposit-controlling amount of the fuel
09 additive composition of the present invention.

10

11 The present invention additionally provides a fuel
12 concentrate comprising an inert stable oleophilic
13 organic solvent boiling in the range of from about
14 150°F. to 400°F. and from about 10 to 70 weight percent
15 of the fuel additive composition of the present
16 invention.

17

18 Among other factors, the present invention is based on
19 the surprising discovery that the unique combination of
20 certain polyalkylphenoxyaminoalkanes with
21 poly(oxyalkylene) amines provides excellent control of
22 engine deposits, especially on intake valves, when
23 employed as additives in fuel compositions.

24

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-8-

01 DETAILED DESCRIPTION OF THE INVENTION

02

03 The Polyalkylphenoxyaminoalkane

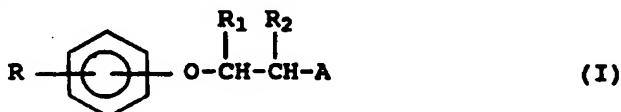
04

05 The polyalkylphenoxyaminoalkane component of the present
06 additive composition has the general formula:

07

08

09



10

11

12 wherein R, R₁, R₂ and A are as defined above.

13

14 Preferably, R is a polyalkyl group having an average
15 molecular weight in the range of about 600 to 3,000, more
16 preferably about 700 to 3,000, and most preferably about 900
17 to 2,500.

18

19 Preferably, one of R₁ and R₂ is hydrogen or lower alkyl of 1
20 to 4 carbon atoms, and the other is hydrogen. More
21 preferably, one of R₁ and R₂ is hydrogen, methyl or ethyl,
22 and the other is hydrogen. Most preferably, R₂ is hydrogen,
23 methyl or ethyl, and R₁ is hydrogen.

24

25 In general, A is amino, N-alkyl amino having from about 1 to
26 about 20 carbon atoms in the alkyl group, preferably about 1
27 to about 6 carbon atoms, more preferably about 1 to about
28 4 carbon atoms; N,N-dialkyl amino having from about 1 to
29 about 20 carbon atoms in each alkyl group, preferably about
30 1 to about 6 carbon atoms, more preferably about 1 to about
31 4 carbon atoms; or a polyamine moiety having from about 2 to
32 about 12 amine nitrogen atoms and from about 2 to about
33 12 carbon atoms.

34

-9-

01 40 carbon atoms, preferably about 2 to 12 amino nitrogen
02 atoms and about 2 to 24 carbon atoms. More preferably, A is
03 amino or a polyamine moiety derived from a polyalkylene
04 polyamine, including alkylene diamine. Most preferably, A
05 is amino or a polyamine moiety derived from ethylene diamine
06 or diethylene triamine.

07

08 It is preferred that the R substituent is located at the
09 meta or, more preferably, the para position on the aromatic
10 ring, i.e., para or meta relative to the ether group.

11

12 The compounds employed in the present invention will
13 generally have a sufficient molecular weight so as to be
14 non-volatile at normal engine intake valve operating
15 temperatures (about 200°-250°C.). Typically, the molecular
16 weight of the compounds employed in this invention will
17 range from about 700 to about 3,500, preferably from about
18 700 to about 2,500.

19

20 Fuel-soluble salts of the compounds of formula I can be
21 readily prepared for those compounds containing an amino or
22 substituted amino group and such salts are contemplated to
23 be useful for preventing or controlling engine deposits.
24 Suitable salts include, for example, those obtained by
25 protonating the amino moiety with a strong organic acid,
26 such as an alkyl- or arylsulfonic acid. Preferred salts are
27 derived from toluenesulfonic acid and methanesulfonic acid.

28

29 Definitions

30

31 As used herein, the following terms have the following
32 meanings unless expressly stated to the contrary.

33

34

-10-

- 01 The term "amino" refers to the group: -NH₂.
- 02
- 03 The term "N-alkylamino" refers to the group: -NHR_a wherein
04 R_a is an alkyl group. The term "N,N-dialkylamino" refers to
05 the group: —NR_bR_c, wherein R_b and R_c are alkyl groups.
- 06
- 07 The term "hydrocarbyl" refers to an organic radical
08 primarily composed of carbon and hydrogen which may be
09 aliphatic, alicyclic, aromatic or combinations thereof,
10 e.g., aralkyl or alkaryl. Such hydrocarbyl groups are
11 generally free of aliphatic unsaturation, i.e., olefinic or
12 acetylenic unsaturation, but may contain minor amounts of
13 heteroatoms, such as oxygen or nitrogen, or halogens, such
14 as chlorine.
- 15
- 16 The term "alkyl" refers to both straight- and branched-chain
17 alkyl groups.
- 18
- 19 The term "lower alkyl" refers to alkyl groups having 1 to
20 about 6 carbon atoms and includes primary, secondary and
21 tertiary alkyl groups. Typical lower alkyl groups include,
22 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
23 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.
- 24
- 25 The term "polyalkyl" refers to an alkyl group which is
26 generally derived from polyolefins which are polymers or
27 copolymers of mono-olefins, particularly 1-mono-olefins,
28 such as ethylene, propylene, butylene, and the like.
29 Preferably, the mono-olefin employed will have 2 to about
30 24 carbon atoms, and more preferably, about 3 to 12 carbon
31 atoms. More preferred mono-olefins include propylene,
32 butylene, particularly isobutylene, 1-octene and 1-decene.
- 33
- 34

-11-

01 Polyolefins prepared from such mono-olefins include
02 polypropylene, polybutene, especially polyisobutene, and the
03 polyalphaolefins produced from 1-octene and 1-decene.

04

05 The term "fuel" or "hydrocarbon fuel" refers to normally
06 liquid hydrocarbons having boiling points in the range of
07 gasoline and diesel fuels.

08

09 General Synthetic Procedures

10

11 The polyalkylphenoxyaminoalkanes employed in this invention
12 may be prepared by the following general methods and
13 procedures. It should be appreciated that where typical or
14 preferred process conditions (e.g., reaction temperatures,
15 times, mole ratios of reactants, solvents, pressures, etc.)
16 are given, other process conditions may also be used unless
17 otherwise stated. Optimum reaction conditions may vary with
18 the particular reactants or solvents used, but such
19 conditions can be determined by one skilled in the art by
20 routine optimization procedures.

21

22 Those skilled in the art will also recognize that it may be
23 necessary to block or protect certain functional groups
24 while conducting the following synthetic procedures. In
25 such cases, the protecting group will serve to protect the
26 functional group from undesired reactions or to block its
27 undesired reaction with other functional groups or with the
28 reagents used to carry out the desired chemical
29 transformations. The proper choice of a protecting group
30 for a particular functional group will be readily apparent
31 to one skilled in the art. Various protecting groups and
32 their introduction and removal are described, for example,
33 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*
34

-12-

01 Organic Synthesis, Second Edition, Wiley, New York, 1991,
02 and references cited therein.

03

04 Synthesis

05

06 The polyalkylphenoxyaminoalkanes employed in the present
07 invention may be prepared by a process which initially
08 involves hydroxyalkylation of a polyalkylphenol of the
09 formula:

10

11



12

13

14

15 wherein R is as defined herein, with an alkylene carbonate
16 of the formula:

17

18

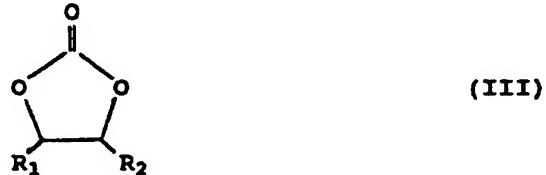
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20

21

22

23



24

25 wherein R₁ and R₂ are as defined herein, in the presence of
26 a catalytic amount of an alkali metal hydride or hydroxide,
27 or alkali metal salt, to provide a polyalkylphenoxyalkanol
28 of the formula:

29

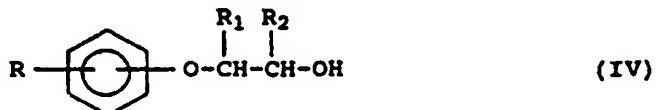
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31

32

33

34 wherein R, R₁ and R₂ are as defined herein.



01
02 The polyalkylphenols of formula II are well known materials
03 and are typically prepared by the alkylation of phenol with
04 the desired polyolefin or chlorinated polyolefin. A further
05 discussion of polyalkylphenols can be found, for example, in
06 U.S. Patent No. 4,744,921 and U.S. Patent No. 5,300,701.

07
08 Accordingly, the polyalkylphenols of formula II may be
09 prepared from the corresponding olefins by conventional
10 procedures. For example, the polyalkylphenols of formula II
11 above may be prepared by reacting the appropriate olefin or
12 olefin mixture with phenol in the presence of an alkylating
13 catalyst at a temperature of from about 25°C. to 150°C., and
14 preferably 30°C. to 100°C. either neat or in an essentially
15 inert solvent at atmospheric pressure. A preferred
16 alkylating catalyst is boron trifluoride. Molar ratios of
17 reactants may be used. Alternatively, molar excesses of
18 phenol can be employed, i.e., 2 to 3 equivalents of phenol
19 for each equivalent of olefin with unreacted phenol
20 recycled. The latter process maximizes monoalkylphenol.
21 Examples of inert solvents include heptane, benzene,
22 toluene, chlorobenzene and 250 thinner which is a mixture of
23 aromatics, paraffins and naphthenes.

24
25 The polyalkyl substituent on the polyalkylphenols employed
26 in the invention is generally derived from polyolefins which
27 are polymers or copolymers of mono-olefins, particularly
28 1-mono-olefins, such as ethylene, propylene, butylene, and
29 the like. Preferably, the mono-olefin employed will have 2
30 to about 24 carbon atoms, and more preferably, about 3 to
31 12 carbon atoms. More preferred mono-olefins include
32 propylene, butylene, particularly isobutylene, 1-octene and
33 1-decene. Polyolefins prepared from such mono-olefins
34 include polypropylene, polybutene, especially polyisobutene,

-14-

01 and the polyalphaolefins produced from 1-octene and
02 1-decene.

03

04 The preferred polyisobutenes used to prepare the presently
05 employed polyalkylphenols are polyisobutenes which comprise
06 at least about 20% of the more reactive methylvinylidene
07 isomer, preferably at least 50% and more preferably at least
08 70%. Suitable polyisobutenes include those prepared using
09 BF_3 catalysts. The preparation of such polyisobutenes in
10 which the methylvinylidene isomer comprises a high
11 percentage of the total composition is described in U.S.
12 Patent Nos. 4,152,499 and 4,605,808. Such polyisobutenes,
13 known as "reactive" polyisobutenes, yield high molecular
14 weight alcohols in which the hydroxyl group is at or near
15 the end of the hydrocarbon chain. Examples of suitable
16 polyisobutenes having a high alkylvinylidene content include
17 Ultravis 30, a polyisobutene having a number average
18 molecular weight of about 1300 and a methylvinylidene
19 content of about 74%, and Ultravis 10, a polyisobutene
20 having a number average molecular weight of about 950 and a
21 methylvinylidene content of about 76%, both available from
22 British Petroleum.

23

24 The alkylene carbonates of formula III are known compounds
25 which are available commercially or can be readily prepared
26 using conventional procedures. Suitable alkylene carbonates
27 include ethylene carbonate, propylene carbonate,
28 1,2-butylene carbonate, 2,3-butylene carbonate, and the
29 like. A preferred alkylene carbonate is ethylene carbonate.

30

31 The catalyst employed in the reaction of the polyalkylphenol
32 and alkylene carbonate may be any of the well known
33 hydroxyalkylation catalysts. Typical hydroxyalkylation
34 catalysts include alkali metal hydrides, such as lithium

-15-

01 hydride, sodium hydride and potassium hydride, alkali metal
02 hydroxides, such as sodium hydroxide and potassium
03 hydroxide, and alkali metal salts, for example, alkali metal
04 halides, such as sodium chloride and potassium chloride, and
05 alkali metal carbonates, such as sodium carbonate and
06 potassium carbonate. The amount of catalyst employed will
07 generally range from about 0.01 to 1.0 equivalent,
08 preferably from about 0.05 to 0.3 equivalent.

09

10 The polyalkylphenol and alkylene carbonate are generally
11 reacted in essentially equivalent amounts in the presence of
12 the hydroxyalkylation catalyst at a temperature in the range
13 of about 100°C. to 210°C., and preferably from about 150°C.
14 to about 170°C. The reaction may take place in the presence
15 or absence of an inert solvent.

16

17 The time of reaction will vary depending on the particular
18 alkylphenol and alkylene carbonate reactants, the catalyst
19 used and the reaction temperature. Generally, the reaction
20 time will range from about two hours to about five hours.
21 The progress of the reaction is typically monitored by the
22 evolution of carbon dioxide. At the completion of the
23 reaction, the polyalkylphenoxyalkanol product is isolated
24 using conventional techniques.

25

26 The hydroxyalkylation reaction of phenols with alkylene
27 carbonates is well known in the art and is described, for
28 example, in U.S. Patent Nos. 2,987,555; 2,967,892; 3,283,030
29 and 4,341,905.

30

31

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-16-

01 Alternatively, the polyalkylphenoxyalkanol product of
02 formula IV may be prepared by reacting the polyalkylphenol
03 of formula II with an alkylene oxide of the formula:

04

05



06

07

08 10 wherein R₁ and R₂ are as defined herein, in the presence of
11 a hydroxyalkylation catalyst as described above.

12

13 Suitable alkylene oxides of formula V include ethylene
14 oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene
15 oxide, and the like. A preferred alkylene oxide is ethylene
16 oxide.

17

18 In a manner similar to the reaction with alkylene carbonate,
19 the polyalkylphenol and alkylene oxide are reacted in
20 essentially equivalent or equimolar amounts in the presence
21 of 0.01 to 1.0 equivalent of a hydroxyalkylation catalyst,
22 such as sodium or potassium hydride, at a temperature in the
23 range of about 30°C. to about 150°C., for about 2 to about
24 24 hours. The reaction may be conducted in the presence or
25 absence of a substantially anhydrous inert solvent.

26

Suitable solvents include toluene, xylene, and the like.
27 Generally, the reaction is conducted at a pressure
28 sufficient to contain the reactants and any solvent present,
29 typically at atmospheric or higher pressure. Upon
30 completion of the reaction, the polyalkylphenoxyalkanol is
31 isolated by conventional procedures.

32

33

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-17-

01 The polyalkylphenoxyalkanol of formula IV is subsequently
02 reacted, either directly or through an intermediate, with an
03 appropriate amine to provide the desired
04 polyalkylphenoxyaminoalkanes of formula I. Suitable amine
05 reactants which may be employed to form the amine component,
06 i.e., substituent A, of the polyalkylphenoxyaminoalkanes
07 employed in the present invention are discussed more fully
08 below.

09

10 The Amine Component of the Polyalkylphenoxyaminoalkane

11

12 In general, the amine component of the presently employed
13 polyalkylphenoxyaminoalkanes will contain an average of at
14 least about one basic nitrogen atom per molecule. A "basic
15 nitrogen atom" is one that is titratable by a strong acid,
16 for example, a primary, secondary, or tertiary amine
17 nitrogen; as distinguished from, for example, an carbamyl
18 nitrogen, e.g., $-\text{OC}(\text{O})\text{NH}-$, which is not titratable with a
19 strong acid. Preferably, at least one of the basic nitrogen
20 atoms of the amine component will be primary or secondary
21 amine nitrogen, more preferably, at least one will be a
22 primary amine nitrogen.

23

24 The amine component of the polyalkylphenoxyaminoalkanes
25 employed in this invention is preferably derived from
26 ammonia, a primary alkyl or secondary dialkyl monoamine, or
27 a polyamine having a terminal amino nitrogen atom.

28

29 Primary alkyl monoamines useful in preparing compounds
30 employed in the present invention contain 1 nitrogen atom
31 and from about 1 to about 20 carbon atoms, more preferably
32 about 1 to 6 carbon atoms, most preferably 1 to 4 carbon
33 atoms. Examples of suitable monoamines include
34 N-methylamine, N-ethylamine, N-n-propylamine,

-18-

01 *N-isopropylamine, N-n-butylamine, N-isobutylamine,*
02 *N-sec-butylamine, N-tert-butylamine, N-n-pentylamine,*
03 *N-cyclopentylamine, N-n-hexylamine, N-cyclohexylamine,*
04 *N-octylamine, N-decylamine, N-dodecylamine,*
05 *N-octadecylamine, N-benzylamine, N-(2-phenylethyl)amine,*
06 *2-aminoethanol, 3-amino-1-propanol,*
07 *2-(2-aminoethoxy)ethanol, N-(2-methoxyethyl)amine,*
08 *N-(2-ethoxyethyl)amine and the like. Preferred primary*
09 *amines are N-methylamine, N-ethylamine and N-n-propylamine.*

10
11 The amine component of the presently employed
12 polyalkylphenoxyaminoalkanes may also be derived from a
13 secondary dialkyl monoamine. The alkyl groups of the
14 secondary amine may be the same or different and will
15 generally each contain about 1 to about 20 carbon atoms,
16 more preferably about 1 to about 6 carbon atoms, most
17 preferably about 1 to about 4 carbon atoms. One or both of
18 the alkyl groups may also contain one or more oxygen atoms.
19

20 Preferably, the alkyl groups of the secondary amine are
21 independently selected from the group consisting of methyl,
22 ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl and
23 2-methoxyethyl. More preferably, the alkyl groups are
24 methyl, ethyl or propyl.

25
26 Typical secondary amines which may be used in this invention
27 include *N,N-dimethylamine, N,N-diethylamine,*
28 *N,N-di-n-propylamine, N,N-diisopropylamine,*
29 *N,N-di-n-butylamine, N,N-di-sec-butylamine,*
30 *N,N-di-n-pentylamine, N,N-di-n-hexylamine,*
31 *N,N-dicyclohexylamine, N,N-dioctylamine,*
32 *N-ethyl-N-methylamine, N-methyl-N-n-propylamine,*
33 *N-n-butyl-N-methylamine, N-methyl-N-octylamine,*
34 *N-ethyl-N-isopropylamine, N-ethyl-N-octylamine,*

-19-

01 N,N-di(2-hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine,
02 N,N-di(ethoxyethyl)amine, N,N-di(propoxymethyl)amine and the
03 like. Preferred secondary amines are N,N-dimethylamine,
04 N,N-diethylamine and N,N-di-n-propylamine.

05

06 Cyclic secondary amines may also be employed to form the
07 additives employed in this invention. In such cyclic
08 compounds, the alkyl groups, when taken together, form one
09 or more 5- or 6-membered rings containing up to about
10 20 carbon atoms. The ring containing the amine nitrogen
11 atom is generally saturated, but may be fused to one or more
12 saturated or unsaturated rings. The rings may be
13 substituted with hydrocarbyl groups of from 1 to about
14 10 carbon atoms and may contain one or more oxygen atoms.

15

16 Suitable cyclic secondary amines include piperidine,
17 4-methylpiperidine, pyrrolidine, morpholine,
18 2,6-dimethylmorpholine and the like.

19

20 Suitable polyamines can have a straight- or branched-chain
21 structure and may be cyclic or acyclic or combinations
22 thereof. Generally, the amine nitrogen atoms of such
23 polyamines will be separated from one another by at least
24 two carbon atoms, i.e., polyamines having an aminal
25 structure are not suitable. The polyamine may also contain
26 one or more oxygen atoms, typically present as an ether or a
27 hydroxyl group. Polyamines having a carbon-to-nitrogen ratio
28 of from about 1:1 to about 10:1 are particularly preferred.

29

30 In preparing polyalkylphenoxyaminoalkane compounds using a
31 polyamine where the various nitrogen atoms of the polyamine
32 are not geometrically equivalent, several substitutional
33 isomers are possible and each of these possible isomers is
34 encompassed within this invention.

-20-

01 A particularly preferred group of polyamines for use in the
02 present invention are polyalkylene polyamines, including
03 alkylene diamines. Such polyalkylene polyamines will
04 typically contain from about 2 to about 12 nitrogen atoms
05 and from about 2 to about 40 carbon atoms, preferably about
06 2 to 24 carbon atoms. Preferably, the alkylene groups of
07 such polyalkylene polyamines will contain from about 2 to
08 about 6 carbon atoms, more preferably from about 2 to about
09 4 carbon atoms.

10

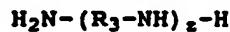
11 Examples of suitable polyalkylene polyamines include
12 ethylenediamine, propylenediamine, isopropylenediamine,
13 butylenediamine, pentylenediamine, hexylenediamine,
14 diethylenetriamine, dipropylenetriamine,
15 dimethylaminopropylamine, diisopropylenetriamine,
16 dibutylenetriamine, di-sec-butylbenzene,
17 triethylenetetraamine, tripropylenetetraamine,
18 triisobutylenetetraamine, tetraethylpentamine,
19 pentaethylenehexamine, dimethylaminopropylamine, and
20 mixtures thereof.

21

22 Particularly suitable polyalkylene polyamines are those
23 having the formula:

24

25



26

27

28

29 wherein R_3 is a straight- or branched-chain alkylene group
30 having from about 2 to about 6 carbon atoms, preferably from
31 about 2 to about 4 carbon atoms, most preferably about
32 2 carbon atoms, i.e., ethylene ($-\text{CH}_2\text{CH}_2-$); and z is an
33 integer from about 1 to about 4, preferably about 1 or
34 about 2.

-21-

01 Particularly preferred polyalkylene polyamines are
02 ethylenediamine, diethylenetriamine, triethylenetetraamine,
03 and tetraethylenepentamine. Most preferred are
04 ethylenediamine and diethylenetriamine, especially
05 ethylenediamine.
06
07 Also contemplated for use in the present invention are
08 cyclic polyamines having one or more 5- to 6-membered rings.
09 Such cyclic polyamines compounds include piperazine,
10 2-methylpiperazine, N-(2-aminoethyl)piperazine,
11 N-(2-hydroxyethyl)piperazine, 1,2-bis-(N-piperazinyl)ethane,
12 3-aminopyrrolidine, N-(2-aminoethyl)pyrrolidine, and the
13 like. Among the cyclic polyamines, the piperazines are
14 preferred.
15
16 Many of the polyamines suitable for use in the present
17 invention are commercially available and others may be
18 prepared by methods which are well known in the art. For
19 example, methods for preparing amines and their reactions
20 are detailed in Sidgewick's "The Organic Chemistry of
21 Nitrogen", Clarendon Press, Oxford, 1966; Noller's
22 "Chemistry of Organic Compounds", Saunders, Philadelphia,
23 2nd Ed., 1957; and Kirk-Othmer's "Encyclopedia of Chemical
24 Technology", 2nd Ed., especially Volume 2, pp. 99-116.
25
26 Preparation of the Polyalkylphenoxyaminoalkane
27
28 As noted above, the polyalkylphenoxyaminoalkanes employed in
29 the present invention may be conveniently prepared by
30 reacting the polyalkylphenoxyalkanol of formula IV, either
31 directly or through an intermediate, with a nitrogen-
32 containing compound, such as ammonia, a primary or secondary
33 alkyl monoamine, or a polyamine, as described herein.
34

-22-

01 Accordingly, the polyalkylphenoxyalkanol of formula IV may
02 be converted to the desired polyalkylphenoxyaminoalkane by a
03 variety of procedures known in the art.

04

05 For example, the terminal hydroxy group on the
06 polyalkylphenoxyalkanol may first be converted to a suitable
07 leaving group, such as a mesylate, chloride or bromide, and
08 the like, by reaction with a suitable reagent, such as
09 methanesulfonyl chloride. The resulting
10 polyalkylphenoxyalkyl mesylate or equivalent intermediate
11 may then be converted to a phthalimide derivative by
12 reaction with potassium phthalimide in the presence of a
13 suitable solvent, such as *N,N*-dimethylformamide. The
14 polyalkylphenoxyalkyl phthalimide derivative is subsequently
15 converted to the desired polyalkylphenoxyaminoalkane by
16 reaction with a suitable amine, such as hydrazine.

17 Alternatively, the leaving group can be converted to an
18 azide, as described, for example, in Turnbull Scriven,
19 Chemical Reviews, Volume 88, pages 297-368, 1988. The azide
20 is subsequently converted to the desired
21 polyalkylphenoxyaminoalkane by reduction with hydrogen and a
22 catalyst, such as palladium on carbon or a Lindlar catalyst.

23

24 The polyalkylphenoxyalkanol of formula IV may also be
25 converted to the corresponding polyalkylphenoxyalkyl
26 chloride by reaction with a suitable halogenating agent,
27 such as HCl, thionyl chloride, or epichlorohydrin, followed
28 by displacement of the chloride with a suitable amine, such
29 as ammonia, a primary or secondary alkyl monoamine, or a
30 polyamine, as described, for example, in U.S. Patent
31 No. 4,247,301 to Honnen, the disclosure of which is
32 incorporated herein by reference.

33

34

-23-

01 Alternatively, the polyalkylphenoxyaminoalkanes employed in
02 the present invention may be prepared from the corresponding
03 polyalkylphenoxyalkanol by a process commonly referred to as
04 reductive amination, such as described in U.S. Patent
05 No. 5,112,364 to Rath et al. and U.S. Patent No. 4,332,595
06 to Herbstman et al., the disclosures of which are
07 incorporated herein by reference.

08

09 In the reductive amination procedure, the
10 polyalkylphenoxyalkanol is aminated with an appropriate
11 amine, such as ammonia or a primary alkyl monoamine, in the
12 presence of hydrogen and a hydrogenation-dehydrogenation
13 catalyst. The amination reaction is typically carried out
14 at temperatures in the range of about 160°C to about 250°C
15 and pressures of about 1,000 to about 5,000 psig, preferably
16 about 1,500 to about 3,000 psig. Suitable hydrogenation-
17 dehydrogenation catalysts include those containing platinum,
18 palladium, cobalt, nickel, copper, or chromium, or mixtures
19 thereof. Generally, an excess of the ammonia or amine
20 reactant is used, such as about a 5-fold to about 60-fold
21 molar excess, and preferably about a 10-fold to about
22 40-fold molar excess, of ammonia or amine.

23

24 When the reductive amination is carried out with a polyamine
25 reactant, the amination is preferably conducted using a two-
26 step procedure as described in commonly-assigned copending
27 U.S. Patent application Serial No. 08/574,485, filed
28 December 19, 1995, and titled, "Reductive Amination Process
29 for Manufacturing a Fuel Additive From Polyoxybutylene
30 Alcohol with Ethylene Diamine", the disclosure of which is
31 incorporated herein by reference in its entirety. According
32 to this procedure, an appropriate alcohol is first contacted
33 with a hydrogenation-dehydrogenation catalyst at a
34 temperature of at least 230°C to provide a carbonyl-

-24-

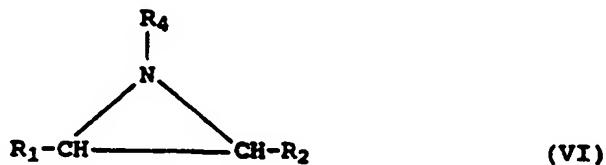
01 containing intermediate, which is subsequently reacted with
02 a polyamine at a temperature below about 190°C in the
03 presence of hydrogen and a hydrogenation catalyst to produce
04 the desired polyamine adduct.

05

06 In an alternative procedure for preparing the
07 polyalkylphenoxyaminoalkanes employed in the present
08 invention, the polyalkylphenol of formula II may be reacted
09 with an aziridine of the formula:

10

11



18 wherein R₁ and R₂ are as defined herein, and R₄ is hydrogen
19 or alkyl of 1 to 20 carbon atoms. A preferred aziridine is
20 one wherein R₁ is hydrogen, R₂ is hydrogen, methyl or ethyl,
21 and R₄ is hydrogen.

22

23 The reaction of aziridines with alcohols to produce beta-
24 amino ethers is well known in the art and is discussed, for
25 example, in Ham and Dermer, "Ethyleneimine and Other
26 Aziridines", Academic Press, New York, 1969, pages 224-227
27 and 256-257.

28

29 The Poly(oxyalkylene) Amine

30

31 The poly(oxyalkylene) amine component of the present fuel
32 additive composition is a poly(oxyalkylene) amine having at
33 least one basic nitrogen atom and a sufficient number of
34 oxyalkylene units to render the poly(oxyalkylene) amine

-25-

01 soluble in hydrocarbons boiling in the gasoline or diesel
02 range.

03
04 Preferably, such poly(oxyalkylene) amines will also be of
05 sufficient molecular weight so as to be nonvolatile at
06 normal engine intake valve operating temperatures, which are
07 generally in the range of about 200°C to 250°C.
08

09 Generally, the poly(oxyalkylene) amines suitable for use in
10 the present invention will contain at least about
11 5 oxyalkylene units, preferably about 5 to 100, more
12 preferably about 8 to 100, and even more preferably about 10
13 to 100. Especially preferred poly(oxyalkylene) amines will
14 contain about 10 to 25 oxyalkylene units.
15

16 The molecular weight of the presently employed
17 poly(oxyalkylene) amines will generally range from about 500
18 to about 10,000, preferably from about 500 to about 5,000.
19

20 Suitable poly(oxyalkylene) amine compounds for use in the
21 present invention include hydrocarbyl poly(oxyalkylene)
22 polyamines as disclosed, for example, in U.S. Patent
23 No. 4,247,301, issued January 27, 1981 to Honnen, the
24 disclosure of which is incorporated herein by reference.
25 These compounds are hydrocarbyl poly(oxyalkylene) polyamines
26 wherein the poly(oxyalkylene) moiety comprises at least one
27 hydrocarbyl-terminated poly(oxyalkylene) chain of 2 to
28 5 carbon atom oxyalkylene units, and wherein the
29 poly(oxyalkylene) chain is bonded through a terminal carbon
30 atom to a nitrogen atom of a polyamine having from 2 to
31 about 12 amine nitrogen atoms and from 2 to about 40 carbon
32 atoms with a carbon-to-nitrogen ratio between about 1:1 and
33 10:1. The hydrocarbyl group on these hydrocarbyl
34 poly(oxyalkylene) polyamines will contain from about 1 to

-26-

01 30 carbon atoms. These compounds generally have molecular
02 weights in the range of about 500 to 10,000, preferably from
03 about 500 to 5,000 and more preferably from about 800 to
04 5,000.

05
06 The above-described hydrocarbyl poly(oxyalkylene) polyamines
07 are prepared by conventional procedures known in the art, as
08 taught, for example, in U.S. Patent No. 4,247,301.

09
10 Other poly(oxyalkylene) amines suitable for use in the
11 present invention are the poly(oxyalkylene) polyamines
12 wherein the poly(oxyalkylene) moiety is connected to the
13 polyamine moiety through an oxyalkylene hydroxy-type linkage
14 derived from an epihalohydrin, such as epichlorohydrin or
15 epibromohydrin. This type of poly(oxyalkylene) amine having
16 an epihalohydrin-derived linkage is described, for example,
17 in U.S. Patent No. 4,261,704, issued April 14, 1981 to
18 Langdon, the disclosure of which is incorporated herein by
19 reference.

20
21 Useful polyamines for preparing the epihalohydrin-derived
22 poly(oxyalkylene) polyamines include, for example, alkylene
23 polyamines, polyalkylene polyamines, cyclic amines, such as
24 piperazines, and amino-substituted amines. The
25 poly(oxyalkylene) polyamines having an epihalohydrin-derived
26 linkage between the poly(oxyalkylene) and polyamine moieties
27 are prepared using known procedures as taught, for example,
28 in U.S. Patent No. 4,261,704.

29
30 Another type of poly(oxyalkylene) amine useful in the
31 present invention is a highly branched alkyl
32 poly(oxyalkylene) monoamine as described, for example in
33 U.S. Patent No. 5,094,667, issued March 10, 1992 to
34 Schilowitz et al., the disclosure of which is incorporated

-27-

01 herein by reference. These highly branched alkyl
02 poly(oxyalkylene) monoamines have the general formula:

03

04



05

06

07

08 wherein R_4 is a highly branched alkyl group containing from
09 12 to 40 carbon atoms, preferably an alkyl group having
10 20 carbon atoms which is derived from a Guerbet condensation
11 reaction, and p is a number up to 30, preferably 4 to 8.
12 The preferred alkyl group is derived from a Guerbet alcohol
13 containing 20 carbon atoms having the formula:

14

15

16

17



18

19 wherein R_5 is a hydrocarbyl chain.

20

21 The above highly branched alkyl poly(oxyalkylene) monoamines
22 are prepared by using known methods as disclosed, for
23 example, in U.S. Patent No. 5,094,667.

24

25 A preferred class of poly(oxyalkylene) amine for use in the
26 fuel additive composition of the present invention are
27 hydrocarbyl poly(oxyalkylene) monoamines as described, for
28 example, in U.S. Patent No. 5,112,364, issued May 12, 1992
29 to Rath et al., the disclosure of which is incorporated
30 herein by reference. As disclosed in U.S. Patent
31 No. 5,112,364, such poly(oxyalkylene) monoamines may be
32 prepared by the reductive amination of a phenol-initiated or
33 alkylphenol-initiated poly(oxyalkylene) alcohol with ammonia
34 or a primary amine.

-28-

01 In addition, the above-mentioned U.S. Patent No. 4,247,301
02 to Honnen discloses hydrocarbyl poly(oxyalkylene) monoamines
03 which are suitable for use in the present fuel additive
04 composition. In particular, Example 6 of this patent
05 describes alkylphenyl poly(oxyalkylene) monoamines prepared
06 from ammonia and dimethylamine.

07

08 A particularly preferred type of hydrocarbyl
09 poly(oxyalkylene) monoamine is an alkylphenyl
10 poly(oxyalkylene) monoamine wherein the poly(oxyalkylene)
11 moiety contains oxypropylene units or oxybutylene units or
12 mixtures of oxypropylene and oxybutylene units. Preferably,
13 the alkyl group on the alkylphenyl moiety is a straight or
14 branched-chain alkyl of 1 to 24 carbon atoms. An especially
15 preferred alkylphenyl moiety is tetrapropenylphenyl, that
16 is, where the alkyl group is a branched-chain alkyl of
17 12 carbon atoms derived from propylene tetramer.

18

19 A further discussion of the hydrocarbon-substituted
20 poly(oxyalkylene) moiety on the poly(oxyalkylene) amine
21 component of the present fuel additive composition is found
22 hereinbelow.

23

24 Another preferred class of poly(oxyalkylene) amine for use
25 in the fuel additive composition of the present invention
26 are hydrocarbyl-substituted poly(oxyalkylene)
27 aminocarbamates disclosed, for example, in U.S. Patent
28 Nos. 4,288,612; 4,236,020; 4,160,648; 4,191,537; 4,270,930;
29 4,233,168; 4,197,409; 4,243,798 and 4,881,945, the
30 disclosure of each of which are incorporated herein by
31 reference.

32

33 These hydrocarbyl poly(oxyalkylene) aminocarbamates contain
34 at least one basic nitrogen atom and have an average

01 molecular weight of about 500 to 10,000, preferably about
02 500 to 5,000, and more preferably about 1,000 to 3,000. As
03 described more fully hereinbelow, these hydrocarbyl
04 poly(oxyalkylene) aminocarbamates contain (a) a
05 poly(oxyalkylene) moiety, (b) an amine moiety and (c) a
06 carbamate connecting group.

07

08 A. The Poly(oxyalkylene) Moiety

09

10 The hydrocarbyl-terminated poly(oxyalkylene) polymers which
11 are utilized in preparing the hydrocarbyl poly(oxyalkylene)
12 aminocarbamates employed in the present invention are
13 monohydroxy compounds, e.g., alcohols, often termed
14 monohydroxy polyethers, or polyalkylene glycol monocarbyl
15 ethers, or "capped" poly(oxyalkylene) glycols, and are to be
16 distinguished from the poly(oxyalkylene) glycols (diols), or
17 polyols, which are not hydrocarbyl-terminated, i.e., are not
18 capped. These hydrocarbyl poly(oxyalkylene) alcohols may be
19 produced by the addition of lower alkylene oxides, such as
20 ethylene oxide, propylene oxide, butylene oxide, etc. to a
21 hydroxy compound, R_9OH , under polymerization conditions,
22 wherein R_9 is the hydrocarbyl group which caps the
23 poly(oxyalkylene) chain.

24

25 In the hydrocarbyl poly(oxyalkylene) aminocarbamates
26 employed in the present invention, the hydrocarbyl group R_9
27 will generally contain from 1 to about 30 carbon atoms,
28 preferably from 2 to about 20 carbon atoms and is preferably
29 aliphatic or aromatic, i.e., an alkyl or alkyl phenyl
30 wherein the alkyl is a straight or branched-chain of from
31 1 to about 24 carbon atoms. More preferably, R_9 is
32 alkylphenyl wherein the alkyl group is a branched-chain of
33 12 carbon atoms, derived from propylene tetramer, and
34 commonly referred to as tetrapropenyl.

-30-

01
02 The oxyalkylene units in the poly(oxyalkylene) moiety
03 preferably contain from 2 to about 5 carbon atoms but one or
04 more units of a larger carbon number may also be present.
05 Generally, each poly(oxyalkylene) polymer contains at least
06 about 5 oxyalkylene units, preferably about 5 to about
07 100 oxyalkylene units, more preferably about 8 to about
08 100 units, even more preferably about 10 to 100 units, and
09 most preferably 10 to about 25 such units. The
10 poly(oxyalkylene) moiety of the hydrocarbyl
11 poly(oxyalkylene) aminocarbamates employed in the present
12 invention is more fully described and exemplified in U.S.
13 Patent No. 4,191,537, issued March 4, 1980 to Lewis, the
14 disclosure of which is incorporated herein by reference.
15
16 Although the hydrocarbyl group on the hydrocarbyl
17 poly(oxyalkylene) moiety will preferably contain from 1 to
18 about 30 carbon atoms, longer hydrocarbyl groups,
19 particularly longer chain alkyl phenyl groups, may also be
20 employed. For example, alkylphenyl poly(oxyalkylene)
21 aminocarbamates wherein the alkyl group contains at least
22 40 carbon atoms, as described in U.S. Patent No. 4,881,945,
23 issued November 21, 1989 to Buckley, are also contemplated
24 for use in the present invention. The alkyl phenyl group on
25 the aminocarbamates of U.S. Patent No. 4,881,945 will
26 preferably contain an alkyl group of 50 to 200 carbon atoms,
27 and more preferably, an alkyl group of 60 to 100 carbon
28 atoms. These longer chain alkyl groups will generally be
29 derived from olefin polymers, such as polybutene. The
30 disclosure of U.S. Patent No. 4,881,945 is incorporated
31 herein by reference.
32
33 Also contemplated for use in the present invention are
34 alkylphenyl poly(oxypropylene) aminocarbamates wherein the

01 alkyl group is a substantially straight-chain alkyl group
02 of about 25 to 50 carbon atoms derived from an alpha olefin
03 oligomer of C₈ to C₂₀ alpha olefins, as described in
04 PCT International Patent Application Publication
05 No. WO 90/07564, published July 12, 1990, the disclosure of
06 which is incorporated herein by reference.

07

08 B. The Amine Moiety

09

10 The amine moiety of the hydrocarbyl poly(oxyalkylene)
11 aminocarbamate is preferably derived from a polyamine having
12 from 2 to about 12 amine nitrogen atoms and from 2 to about
13 40 carbon atoms.

14

15 The polyamine is preferably reacted with a hydrocarbyl
16 poly(oxyalkylene) chloroformate to produce the hydrocarbyl
17 poly(oxyalkylene) aminocarbamate fuel additive finding use
18 within the scope of the present invention. The
19 chloroformate is itself derived from the hydrocarbyl
20 poly(oxyalkylene) alcohol by reaction with phosgene.

21

22 The polyamine provides the hydrocarbyl poly(oxyalkylene)
23 aminocarbamate with, on the average, at least about one
24 basic nitrogen atom per carbamate molecule, i.e., a nitrogen
25 atom titratable by strong acid. The polyamine preferably
26 has a carbon-to-nitrogen ratio of from about 1:1 to about
27 10:1. The polyamine may be substituted with substituents
28 selected from hydrogen, hydrocarbyl groups of from 1 to
29 about 10 carbon atoms, acyl groups of from 2 to about
30 10 carbon atoms, and monoketone, monohydroxy, mononitro,
31 monocyno, alkyl and alkoxy derivatives of hydrocarbyl
32 groups of from 1 to 10 carbon atoms. It is preferred that
33 at least one of the basic nitrogen atoms of the polyamine is
34 a primary or secondary amino nitrogen. The amine moiety of

-32-

01 the hydrocarbyl poly(oxyalkylene) aminocarbamates employed
02 in the present invention has been described and exemplified
03 more fully in U.S. Patent No. 4,191,537.

04

05 A more preferred polyamine for use in preparing the
06 hydrocarbyl poly(oxyalkylene) aminocarbamates finding use
07 within the scope of the present invention is a polyalkylene
08 polyamine, including alkylenediamine, and including
09 substituted polyamines, e.g., alkyl and hydroxyalkyl-
10 substituted polyalkylene polyamine. Preferably, the
11 alkylene group contains from 2 to 6 carbon atoms, there
12 being preferably from 2 to 3 carbon atoms between the
13 nitrogen atoms. Examples of such polyamines include
14 ethylenediamine, diethylenetriamine, triethylenetetramine,
15 di(trimethylene)triamine, dipropylenetriamine,
16 tetraethylenepentamine, etc.

17

18 Among the polyalkylene polyamines, polyethylene polyamine
19 and polypropylene polyamine containing 2 to about 12 amine
20 nitrogen atoms and 2 to about 24 carbon atoms are especially
21 preferred and in particular, the lower polyalkylene
22 polyamines, e.g., ethylenediamine, diethylenetriamine,
23 propylenediamine, dipropylenetriamine, etc., are most
24 preferred.

25

26 C. The Aminocarbamate Connecting Group

27

28 The hydrocarbyl poly(oxyalkylene) aminocarbamate employed as
29 the poly(oxyalkylene) amine component of the fuel additive
30 composition of the present invention is obtained by linking

31

32

33

34

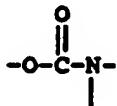
-33-

01 the polyamine and the hydrocarbyl poly(oxyalkylene) alcohol
02 together through a carbamate linkage, i.e.,

03

04

05



06

07

08 wherein the oxygen may be regarded as the terminal hydroxyl
09 oxygen of the poly(oxyalkylene) alcohol, the nitrogen is
10 derived from the polyamine and the carbonyl group $-\text{C}(\text{O})-$, is
11 preferably provided by a coupling agent, such as phosgene.
12

13

14 In a preferred method of preparation, the hydrocarbyl
15 poly(oxyalkylene) alcohol is reacted with phosgene to
16 produce a chloroformate and the chloroformate is reacted
17 with the polyamine. Since there may be more than one
18 nitrogen atom of the polyamine which is capable of reacting
19 with the chloroformate, the carbamate product may contain
20 more than one hydrocarbyl poly(oxyalkylene) moiety. It is
21 preferred that the hydrocarbyl poly(oxyalkylene)
22 aminocarbamate product contains on the average, about
23 one poly(oxyalkylene) moiety per molecule (i.e., is a
24 monocarbamate), although it is understood that this reaction
25 route may lead to mixtures containing appreciable amounts of
26 di- or higher poly(oxyalkylene) chain substitution on a
27 polyamine containing several reactive nitrogen atoms.
28

29

30 A particularly preferred aminocarbamate is alkylphenyl
31 poly(oxybutylene) aminocarbamate, wherein the amine moiety
32 is derived from ethylene diamine or diethylene triamine.
33 Synthetic methods to avoid higher degrees of substitution,
34 methods of preparation, and other characteristics of the

-34-

01 aminocarbamates used in the present invention are more fully
02 described and exemplified in U.S. Patent No. 4,191,537.

03

04 Fuel Compositions

05

06 The fuel additive composition of the present invention will
07 generally be employed in hydrocarbon fuels to prevent and
08 control engine deposits, particularly intake valve
09 deposits. The proper concentration of additive necessary to
10 achieve the desired deposit control varies depending upon
11 the type of fuel employed, the type of engine, and the
12 presence of other fuel additives.

13

14 Generally, the present fuel additive composition will be
15 employed in a hydrocarbon fuel in a concentration ranging
16 from about 50 to about 5,000 parts per million (ppm) by
17 weight, preferably from 100 to 2,500 ppm.

18

19 In terms of individual components, hydrocarbon fuel
20 containing the fuel additive composition of this invention
21 will generally contain about 25 to 2,000 ppm of the
22 polyalkylphenoxyaminoalkane component and about 25 to
23 2,000 ppm of the poly(oxyalkylene) amine component. The
24 ratio of the polyalkylphenoxyaminoalkane to
25 poly(oxyalkylene) amine will generally range from about
26 0.05:1 to about 5:1, and will preferably be about 2:1 or
27 less.

28

29 The fuel additive composition of the present invention may
30 be formulated as a concentrate using an inert stable
31 oleophilic (i.e., dissolves in gasoline) organic solvent
32 boiling in the range of about 150°F. to 400°F. (about 65°C.
33 to 205°C.). Preferably, an aliphatic or an aromatic
34 hydrocarbon solvent is used, such as benzene, toluene,

-35-

01 xylene or higher-boiling aromatics or aromatic thinners.
02 Aliphatic alcohols containing about 3 to 8 carbon atoms,
03 such as isopropanol, isobutylcarbinol, n-butanol and the
04 like, in combination with hydrocarbon solvents are also
05 suitable for use with the present additives. In the
06 concentrate, the amount of the additive will generally range
07 from about 10 to about 70 weight percent, preferably 10 to
08 50 weight percent, more preferably from 20 to 40 weight
09 percent.

10

11 In gasoline fuels, other fuel additives may be employed with
12 the additive composition of the present invention,
13 including, for example, oxygenates, such as t-butyl methyl
14 ether, antiknock agents, such as methylcyclopentadienyl
15 manganese tricarbonyl, and other dispersants/detergents,
16 such as hydrocarbyl amines, or succinimides. Additionally,
17 antioxidants, metal deactivators, demulsifiers and
18 carburetor or fuel injector detergents may be present.

19

20 In diesel fuels, other well-known additives can be employed,
21 such as pour point depressants, flow improvers, cetane
22 improvers, and the like.

23

24 A fuel-soluble, nonvolatile carrier fluid or oil may also be
25 used with the fuel additive composition of this invention.
26 The carrier fluid is a chemically inert hydrocarbon-soluble
27 liquid vehicle which substantially increases the nonvolatile
28 residue (NVR), or solvent-free liquid fraction of the fuel
29 additive composition while not overwhelmingly contributing
30 to octane requirement increase. The carrier fluid may be a
31 natural or synthetic fluid, such as mineral oil, refined
32 petroleum oils, synthetic polyalkanes and alkenes, including
33 hydrogenated and unhydrogenated polyalphaolefins, and
34 synthetic polyoxyalkylene-derived fluids, such as those

-36-

01 described, for example, in U.S. Patent No. 4,191,537 to
02 Lewis, and polyesters, such as those described, for example,
03 in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to
04 Vogel et al., and in European Patent Application
05 Nos. 356,726, published March 7, 1990, and 382,159,
06 published August 16, 1990.

07

08 These carrier fluids are believed to act as a carrier for
09 the fuel additive composition of the present invention and
10 to assist in removing and retarding deposits. The carrier
11 fluid may also exhibit synergistic deposit control
12 properties when used in combination with the fuel additive
13 composition of this invention.

14

15 The carrier fluids are typically employed in amounts ranging
16 from about 25 to about 5000 ppm by weight of the hydrocarbon
17 fuel, preferably from 100 to 3000 ppm of the fuel.
18 Preferably, the ratio of carrier fluid to deposit control
19 additive will range from about 0.2:1 to about 10:1, more
20 preferably from 0.5:1 to 3:1.

21

22 When employed in a fuel concentrate, carrier fluids will
23 generally be present in amounts ranging from about 20 to
24 about 60 weight percent, preferably from 30 to 50 weight
25 percent.

26

PREPARATIONS AND EXAMPLES

27

28 A further understanding of the invention can be had in the
29 following nonlimiting Examples. Wherein unless expressly
30 stated to the contrary, all temperatures and temperature
31 ranges refer to the Centigrade system and the term "ambient"
32 or "room temperature" refers to about 20°C.-25°C. The term
33 "percent" or "%" refers to weight percent and the term
34 "mole" or "moles" refers to gram moles. The term

-37-

01 "equivalent" refers to a quantity of reagent equal in moles,
02 to the moles of the preceding or succeeding reactant recited
03 in that example in terms of finite moles or finite weight or
04 volume. Where given, proton-magnetic resonance spectrum
05 (p.m.r. or n.m.r.) were determined at 300 mHz, signals are
06 assigned as singlets (s), broad singlets (bs), doublets (d),
07 double doublets (dd), triplets (t), double triplets (dt),
08 quartets (q), and multiplets (m), and cps refers to cycles
09 per second.

10

11 Example 1

12

13 Preparation of Polyisobutyl Phenol

14

15 To a flask equipped with a magnetic stirrer, reflux
16 condenser, thermometer, addition funnel and nitrogen inlet
17 was added 203.2 grams of phenol. The phenol was warmed to
18 40°C. and the heat source was removed. Then,
19 73.5 milliliters of boron trifluoride etherate was added
20 dropwise. 1040 grams of Ultravis 10 Polyisobutene
21 (molecular weight 950, 76% methylvinylidene, available from
22 British Petroleum) was dissolved in 1,863 milliliters of
23 hexane. The polyisobutene was added to the reaction at a
24 rate to maintain the temperature between 22°C-27°C. The
25 reaction mixture was stirred for 16 hours at room
26 temperature. Then, 400 milliliters of concentrated ammonium
27 hydroxide was added, followed by 2,000 milliliters of
28 hexane. The reaction mixture was washed with water
29 (3 X 2,000 milliliters), dried over magnesium sulfate,
30 filtered and the solvents removed under vacuum to yield
31 1,056.5 grams of a crude reaction product. The crude
32 reaction product was determined to contain 80% of the

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-38-

01 desired product by proton NMR and chromatography on silica
02 gel eluting with hexane, followed by hexane: ethylacetate:
03 ethanol (93:5:2).

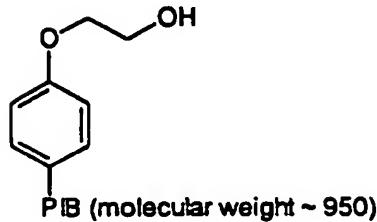
04

05 Example 2

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07 Preparation of

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17 Potassium hydride (1.1 grams of a 35 weight percent
18 dispersion of in mineral oil) and 4- polyisobutyl phenol
19 (99.7 grams, prepared as in Example 1) were added to a flask
20 equipped with a magnetic stirrer, reflux condensor, nitrogen
21 inlet and thermometer. The reaction was heated at 130°C for
22 one hour and then cooled to 100°C. Ethylene carbonate
23 (8.6 grams) was added and the mixture was heated at 160°C
24 for 16 hours. The reaction was cooled to room temperature
25 and one milliliter of isopropanol was added. The reaction
26 was diluted with one liter of hexane, washed three times
27 with water and once with brine. The organic layer was dried
28 over anhydrous magnesium sulfate, filtered and the solvents
29 removed in vacuo to yield 98.0 grams of the desired product
30 as a yellow oil.

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Example 3

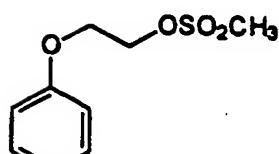
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Preparation of

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PB (molecular weight ~ 950)

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The alcohol from Example 2 (20.0 grams), triethylamine (2.9 mL), and anhydrous dichloromethane (200 mL) were combined. The solution was cooled to 0°C and methanesulfonyl chloride (1.5 mL) was added dropwise. The reaction was stirred at room temperature under nitrogen for 16 hours. The solution was diluted with dichloromethane (600 mL) and was washed twice with saturated aqueous sodium bicarbonate solution and once with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed in vacuo to yield 20.4 grams as a yellow oil.

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Example 4

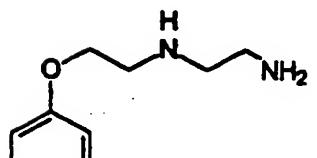
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Preparation of

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PIB (molecular weight ~ 950)

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14 Ethylenediamine (12.3 mL) and anhydrous toluene (100 mL)
15 were combined under nitrogen. The product from Example 3
16 (20.4 grams, dissolved in 100 mL of anhydrous toluene) was
17 added dropwise. The resulting solution was refluxed for
18 16 hours. The solution was diluted with hexane (600 mL) and
19 was washed once with saturated aqueous sodium bicarbonate
20 solution, three times with water and once with brine. The
21 organic layer was dried over anhydrous sodium sulfate,
22 filtered and the solvents removed in vacuo to yield
23 15.1 grams as a yellow oil. The oil was chromatographed on
24 silica gel, eluting with hexane / diethyl ether (50:50) then
25 hexane / diethyl ether / methanol / isopropylamine
26 (40:40:15:5) to yield 10.3 grams of the desired product as a
27 yellow oil. ¹H NMR (CDCL₃) δ 7.25 (d, 2H), 6.8 (d, 2H),
28 4.1 (t, 2H), 3.0 (t, 2H), 2.85 (t, 2H), 2.75 (t, 2H),
29 1.95 (bs, 3H), 1.5-0.7 (m, 137H).

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Example 5

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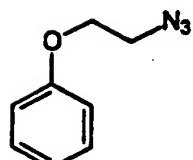
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Preparation of

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PB (molecular weight ~ 950)

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14 A mesylate prepared as described in Example 3 (406.5 grams),
15 sodium azide (198.2 grams), Adogen 464, a methyltrialkyl
16 (C_8-C_{10}) ammonium chloride available from Ashland Chemical
17 (8.0 mL), N,N - dimethylformamide (800 mL) and toluene
18 (1.2 L) were combined. The reaction was refluxed for
19 sixteen hours and cooled to room temperature. The mixture
20 was filtered and the solvent was removed in vacuo. The
21 residue was diluted with hexane (3.0 L) and washed three
22 times with water and once with brine. The organic layer was
23 dried over anhydrous magnesium sulfate, filtered and the
24 solvents removed in vacuo to yield 334.3 grams of the
25 desired azide as a yellow oil.

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Example 6

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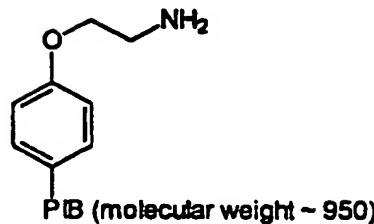
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Preparation of

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14 A solution of the product from Example 5 (334.3 grams) in
15 ethyl acetate (750 mL) and toluene (750 mL), containing
16 10t palladium on charcoal (7.0 grams) was hydrogenolyzed at
17 35-40 psi for 16 hours on a Parr low pressure hydrogenator.
18 Catalyst filtration and removal of the solvent in vacuo
19 yielded 322.3 grams of the desired product as a yellow oil.
20 ^1H NMR (CDCl_3) d 7.25 (d, 2H), 6.8 (d, 2H), 4.0 (t, 1H),
21 3.1 (t, 2H), 2.35 (bs, 2H), 0.7-1.6 (m, 137H).

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Example 6

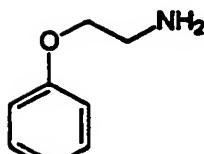
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Preparation of

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PB (molecular weight ~ 950)

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14 A solution of the product from Example 5 (334.3 grams) in
15 ethyl acetate (750 mL) and toluene (750 mL), containing
16 10% palladium on charcoal (7.0 grams) was hydrogenolyzed at
17 35-40 psi for 16 hours on a Parr low pressure hydrogenator.
18 Catalyst filtration and removal of the solvent in vacuo
19 yielded 322.3 grams of the desired product as a yellow oil.
20 ^1H NMR (CDCl_3) d 7.25 (d, 2H), 6.8 (d, 2H), 4.0 (t, 1H),
21 3.1 (t, 2H), 2.35 (bs, 2H), 0.7-1.6 (m, 137H).

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Example 7

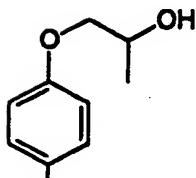
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Preparation of

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PIB (molecular weight ~ 950)

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Potassium hydride (15.1 grams of a 35 weight percent dispersion of in mineral oil) and 4- polyisobutyl phenol (1378.5 grams, prepared as in Example 1) were added to a flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Propylene carbonate (115.7 milliliters) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and ten milliliters of isopropanol were added. The reaction was diluted with ten liters of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 1301.7 grams of the desired product as a yellow oil.

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Example 8

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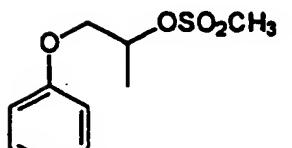
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Preparation of

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PB (molecular weight ~ 950)

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14 The alcohol from Example 7 (50.0 grams), triethylamine
15 (7.0 mL), and anhydrous dichloromethane (500 mL) were
16 combined. The solution was cooled to 0°C and
17 methanesulfonyl chloride (3.7 mL) was added dropwise. The
18 reaction was stirred at room temperature under nitrogen for
19 16 hours. The solution was diluted with dichloromethane
20 (1.5L) and was washed three times with saturated aqueous
21 sodium bicarbonate solution and once with brine. The
22 organic layer was dried over anhydrous sodium sulfate,
23 filtered and the solvents removed in vacuo to yield
24 57.7 grams as a yellow oil.

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Example 9

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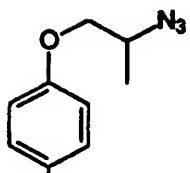
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Preparation of

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PIB (molecular weight ~ 950)

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14 The mesylate from Example 8 (57.7 grams), sodium azide
15 (27.1 grams), Adogen 464 (1.0 mL), N,N - dimethylformamide
16 (400 mL) and toluene (600 mL) were combined. The reaction
17 was refluxed for sixteen hours and cooled to room
18 temperature. The mixture was filtered and the solvent was
19 removed in vacuo. The residue was diluted with hexane
20 (1.5 L) and washed three times with water and once with
21 brine. The organic layer was dried over anhydrous magnesium
22 sulfate, filtered and the solvents removed in vacuo to yield
23 43.1 grams of the desired azide as a yellow oil.

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Example 10

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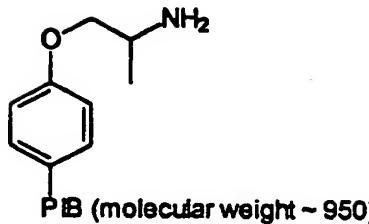
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Preparation of

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14 A solution of the product from Example 9 (43.1 grams) in
15 ethyl acetate (100 mL) and toluene (100 mL), containing
16 10% palladium on charcoal (2.0 grams) was hydrogenolyzed at
17 35-40 psi for 16 hours on a Parr low pressure hydrogenator.
18 Catalyst filtration and removal of the solvent in vacuo
19 yielded 41.5 grams of the desired product as a yellow oil.
20 ^1H NMR (CDCl_3) δ 7.25 (d, 2H), 6.85 (d, 2H), 3.9 (abq, 1H),
21 3.65 (abq, 1H), 3.35 (m, 1H), 1.9 (bs, 2H), 0.7-1.6
22 (m, 14OH).

23

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Example 11

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Preparation of Dodecylphenoxy Poly(oxybutylene)poly(oxypropylene) Amine

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29 A dodecylphenoxy poly(oxybutylene)poly(oxypropylene) amine
30 was prepared by the reductive amination with ammonia of the
31 random copolymer poly(oxyalkylene) alcohol, dodecylphenoxy
32 poly(oxybutylene)poly(oxypropylene) alcohol, wherein the
33 alcohol has an average molecular weight of about 1598. The
34 poly(oxyalkylene) alcohol was prepared from dodecylphenol

-47-

01 using a 75/25 weight/weight ratio of butylene oxide and
02 propylene oxide, in accordance with the procedures described
03 in U.S. Patent Nos. 4,191,537; 2,782,240 and 2,841,479, as
04 well as in Kirk-Othmer, "Encyclopedia of Chemical
05 Technology", 4th edition, Volume 19, 1996, page 722. The
06 reductive amination of the poly(oxyalkylene) alcohol was
07 carried out using conventional techniques as described in
08 U.S. Patent Nos. 5,112,364; 4,609,377 and 3,440,029.

09

10 Example 12

11

12 Single-Cylinder Engine Test

13

14 The test compounds were blended in gasoline and their
15 deposit reducing capacity determined in an ASTM/CFR
16 single-cylinder engine test.

17

18 A Waukesha CFR single-cylinder engine was used. Each run
19 was carried out for 15 hours, at the end of which time the
20 intake valve was removed, washed with hexane and weighed.
21 The previously determined weight of the clean valve was
22 subtracted from the weight of the valve at the end of the
23 run. The differences between the two weights is the weight
24 of the deposit. A lesser amount of deposit indicates a
25 superior additive. The operating conditions of the test
26 were as follows: water jacket temperature 200°F; intake
27 manifold vacuum of 12 in. Hg, air-fuel ratio of 12, ignition
28 spark timing of 40° BTC; engine speed is 1800 rpm; the
29 engine oil is a commercial SAE 30 grade.

30

31 The amount of carbonaceous deposit in milligrams on the
32 intake valves is reported for each of the test compounds in
33 Table I and Table II.

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-48-

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TABLE I

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Intake Valve Deposit Weight
(in milligrams)

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Sample ¹	Run 1	Run 2	Average
Base Fuel	333.5	354.9	344.2
Example 4	22.5	22.7	22.6

¹At 150 parts per million actives (ppma).

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TABLE II

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Sample ¹	Run 1	Run 2	Average
Base Fuel	323.8	312.1	318.0
Example 6	12.1	21.0	16.6

¹At 125 parts per million actives (ppma).

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The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give the concentrations indicated in the tables.

The data in Table I and Table II illustrates the significant reduction in intake valve deposits provided by the polyalkylphenoxyaminoalkanes employed in the present invention (Examples 4 and 6) compared to the base fuel.

-49-

01 The combination of polyalkylphenoxyaminoalkane and
 02 poly(oxyalkylene) amine was also tested in the single-
 03 cylinder engine test and the amount of carbonaceous deposit
 04 in milligrams on the intake valves is reported in Table III.

05

06

07 TABLE III

08

09

10 Intake Valve Deposit Weight
 11 (in milligrams)

12	Sample	Conc. (ppma)	Run 1	Run 2	Average
13	Base Fuel	-	250.3	253.1	251.6
14	Polyalkylphenoxy- aminoalkane/ Carrier Fluid ¹	50/50	188	149.8	169
15	Polyalkylphenoxy- aminoalkane/Poly (oxyalkylene) Amine ²	50/50	9.4	4.1	6.75
16	Polyalkylphenoxy- aminoalkane/ Poly (oxyalkylene) Amine ³	50/50	21.2	14.3	17.8
17	Polyalkylphenoxy- aminoalkane/ Carrier Fluid ⁴	50/50	131.8	111.5	121.6
18	Polyalkylphenoxy- aminoalkane/ Poly (oxyalkylene) Amine ⁵	50/50	0	0	0
19	Polyalkylphenoxy- aminoalkane/ Poly (oxyalkylene) Amine ⁶	50/50	1	1.2	1.1

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¹Mixture of 50 ppma of polyisobutylphenoxyaminoalkane prepared as described in Example 10 and 50 ppm of a dodecylphenyl poly(oxybutylene) alcohol carrier fluid.

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- 01 ²Mixture of 50 ppma of polyisobutylphenoxyaminoalkane
02 prepared as described in Example 10 and 50 ppma of
03 dodacylphenoxypoly(oxybutylene)poly(oxypropylene) amine
04 prepared as described in Example 11.
- 04 ³Mixture of 50 ppma of polyisobutylphenoxyaminoalkane
05 prepared as described in Example 10 and 50 ppma of a
06 dodecylphenyl poly(oxybutylene) ethylene diamine carbamate
07 (molecular weight about 1600), prepared essentially as
08 described in Examples 6-8 of U.S. Patent No. 4,197,537.
- 08 ⁴Mixture of 50 ppma of polyisobutylphenoxyaminoalkane
09 prepared as described in Example 6 and 50 ppm of a
10 dodecylphenylpoly(oxybutylene) alcohol carrier fluid.
- 11 ⁵Mixture of 50 ppma of polyisobutylphenoxyaminoalkane
12 prepared as described in Example 6 and 50 ppma of
13 dodecylphenoxypoly(oxybutylene)poly(oxypropylene) amine
14 prepared as described in Example 11.
- 14 ⁶Mixture of 50 ppma of polyisobutylphenoxyaminoalkane
15 prepared as described in Example 6 and 50 ppma of a
16 dodecylphenyl poly(oxybutylene) ethylene diamine carbamate
17 (molecular weight about 1600), prepared essentially as
18 described in Examples 6-8 of U.S. Patent No. 4,197,537.
- 19 The data in Table III demonstrates that the combination of a
20 polyalkylphenoxyaminoalkane and a poly(oxyalkylene) amine
21 has a beneficial effect and gives significantly better
22 intake valve deposit control than the
23 polyalkylphenoxyaminoalkane component with a carrier fluid.

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01 WHAT IS CLAIMED IS:

02

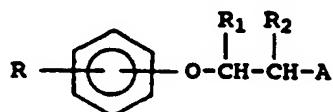
03 1. A fuel additive composition comprising:

04

05 (a) a polyalkylphenoxyaminoalkane compound of the
06 formula:

07

OB



13 or a fuel-soluble salt thereof, wherein R is a
14 polyalkyl group having an average molecular weight
15 in the range of about 600 to 5,000;

R₁ and **R₂** are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

20 A is amino, N-alkyl amino having about 1 to about
21 20 carbon atoms in the alkyl group, N,N-dialkyl
22 amino having about 1 to about 20 carbon atoms in
23 each alkyl group, or a polyamine moiety having
24 about 2 to about 12 amine nitrogen atoms and about
25 2 to about 40 carbon atoms; and

27 (b) a poly(oxyalkylene) amine having at least one
28 basic nitrogen atom and a sufficient number of
29 oxyalkylene units to render the poly(oxyalkylene)
30 amine soluble in hydrocarbons boiling in the
31 gasoline or diesel fuel range.

-52-

- 01 2. The fuel additive composition according to Claim 1,
02 wherein one of R₁ and R₂ is hydrogen or lower alkyl of
03 1 to 4 carbon atoms, and the other is hydrogen.
- 04 3. The fuel additive composition according to Claim 2,
05 wherein one of R₁ and R₂ is hydrogen, methyl or ethyl,
06 and the other is hydrogen.
07
- 08 4. The fuel additive composition according to Claim 3,
09 wherein R₂ is hydrogen, methyl or ethyl, and R₁ is
10 hydrogen.
11
- 12 5. The fuel additive composition according to Claim 1,
13 wherein R is a polyalkyl group having an average
14 molecular weight in the range of about 600 to 3,000.
15
- 16 6. The fuel additive composition according to Claim 5,
17 wherein R is a polyalkyl group having an average
18 molecular weight in the range of about 700 to 3,000.
19
- 20 7. The fuel additive composition according to Claim 6,
21 wherein R is a polyalkyl group having an average
22 molecular weight in the range of about 900 to 2,500.
23
- 24 8. The fuel additive composition according to Claim 1,
25 wherein R is a polyalkyl group derived from
26 polypropylene, polybutene, or a polyalphaolefin
oligomer of 1-octene or 1-decene.
27
- 28 9. The fuel additive composition according to Claim 8,
29 wherein R is a polyalkyl group derived from
30 polyisobutene.
31
- 32
- 33
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-53-

- 01 10. The fuel additive composition according to Claim 9,
02 wherein the polyisobutane contains at least about 20%
03 of a methylvinylidene isomer.
- 04 11. The fuel additive composition according to Claim 1,
05 wherein A is amino, N-alkyl amino or a polyamine
06 moiety.
- 07 12. The fuel additive composition according to Claim 11,
08 wherein A is amino or N-alkyl amino having from about 1
09 to about 4 carbon atoms in the alkyl group.
- 10 13. The fuel additive composition according to Claim 12,
11 wherein A is amino.
- 12 14. The fuel additive composition according to Claim 11,
13 wherein A is a polyamine moiety having from about 2 to
14 about 12 amine nitrogen atoms and from about 2 to about
15 40 carbon atoms.
- 16 15. The fuel additive composition according to Claim 14,
17 wherein A is a polyamine moiety derived from a
18 polyalkylene polyamine containing from about 2 to about
19 12 amine nitrogen polyamine atoms and from about 2 to
20 about 24 carbon atoms.
- 21 16. The fuel additive composition according to Claim 15,
22 wherein the polyalkylene polyamine has the formula:
- 23
- 24
- 25
- 26
- 27
- 28
- 29 $H_2N-(R_3-NH)_z-H$
- 30
- 31 wherein R_3 is an alkylene group having from about 2 to
32 about 6 carbon atoms and z is an integer from about 1
33 to about 4.
- 34

-54-

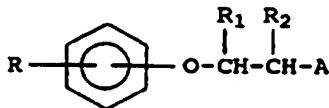
- 01 17. The fuel additive composition according to Claim 16,
02 wherein R₃ is an alkylene group having from about 2 to
03 about 4 carbon atoms.
- 04 18. The fuel additive composition according to Claim 17,
05 wherein the polyalkylene polyamine is ethylene diamine
06 or diethylene triamine.
- 08 19. The fuel additive composition according to Claim 18,
09 wherein the polyalkylene polyamine is ethylene diamine.
- 10
- 11 20. The fuel additive composition according to Claim 1,
12 wherein R is a polyalkyl group derived from
13 polyisobutene, R₁ and R₂ are hydrogen and A is amino or
14 a polyamine moiety derived from ethylene diamine.
- 15
- 16 21. The fuel additive composition according to Claim 1,
17 wherein said poly(oxyalkylene) amine has a molecular
18 weight in the range of about 500 to about 10,000.
- 19
- 20 22. The fuel additive composition according to Claim 1,
21 wherein said poly(oxyalkylene) amine contains at least
22 about 5 oxyalkylene units.
- 23
- 24 23. The fuel additive composition according to Claim 1,
25 wherein said poly(oxyalkylene) amine is a hydrocarbyl
poly(oxyalkylene) polyamine.
- 26
- 27 24. The fuel additive composition according to Claim 1,
28 wherein said poly(oxyalkylene) amine is a hydrocarbyl
poly(oxyalkylene) aminocarbamate.
- 29
- 30 25. The fuel additive composition according to Claim 24,
31 wherein the hydrocarbyl group of said hydrocarbyl
32 poly(oxyalkylene) aminocarbamate contains from 1 to
33 about 30 carbon atoms.
- 34

- 01 26. The fuel additive composition according to Claim 25,
02 wherein said hydrocarbyl group of said hydrocarbyl
03 poly(oxyalkylene) aminocarbamate is an alkylphenyl
04 group.
- 05 27. The fuel additive composition according to Claim 26,
06 wherein the alkyl moiety of said alkylphenyl group is
07 tetrapropenyl.
- 09 28. The fuel additive composition according to Claim 24,
10 wherein the amine moiety of said hydrocarbyl
11 poly(oxyalkylene) aminocarbamate is derived from a
12 polyamine having from 2 to 12 amine nitrogen atoms and
13 from 2 to 40 carbon atoms.
- 15 29. The fuel additive composition according to Claim 28,
16 wherein said polyamine is a polyalkylene polyamine
17 having 2 to 12 amine nitrogen atoms and 2 to 24 carbon
18 atoms.
- 19 30. The fuel additive composition according to Claim 29,
20 wherein said polyalkylene polyamine is selected from
21 the group consisting of ethylenediamine,
22 propylenediamine, diethylenetriamine and
23 dipropylenetriamine.
- 25 31. The fuel additive composition according to Claim 24,
26 wherein the poly(oxyalkylene) moiety of said
27 hydrocarbyl poly(oxyalkylene) aminocarbamate is derived
28 from C₂ to C₅ oxyalkylene units.
- 30 32. The fuel additive composition according to Claim 24,
31 wherein said hydrocarbyl poly(oxyalkylene)
32 aminocarbamate is an alkylphenyl poly(oxybutylene)
33 aminocarbamate, wherein the amine moiety is derived
34 from ethylenediamine or diethylenetriamine.

-56-

- 01 33. The fuel additive composition according to Claim 1,
02 wherein said poly(oxyalkylene) amine is a hydrocarbyl
03 poly(oxyalkylene) monoamine.
- 04 34. The fuel additive composition according to Claim 33,
05 wherein said hydrocarbyl poly(oxyalkylene) monoamine is
06 an alkylphenyl poly(oxyalkylene) monoamine, wherein the
07 poly(oxyalkylene) moiety contains oxypropylene units or
08 oxybutylene units or mixtures thereof.
- 10 35. The fuel additive composition according to Claim 34,
11 wherein the alkylphenyl group is tetrapropenylphenyl.
- 12 36. A fuel composition comprising a major amount of
13 hydrocarbons boiling in the gasoline or diesel range
14 and an effective deposit-controlling amount of a fuel
15 additive composition comprising:

- 17
18 (a) a polyalkylphenoxyaminoalkane compound
19 of the formula:



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or a fuel-soluble salt thereof, wherein R is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000;

R₁ and R₂ are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

- 01 A is amino, N-alkyl amino having about 1 to about
02 20 carbon atoms in the alkyl group, N,N-dialkyl
03 amino having about 1 to about 20 carbon atoms in
04 each alkyl group, or a polyamine moiety having
05 about 2 to about 12 amine nitrogen atoms and about
06 2 to about 40 carbon atoms; and
07
08 (b) a poly(oxyalkylene) amine having at least one
09 basic nitrogen atom and a sufficient number of
10 oxyalkylene units to render the poly(oxyalkylene)
11 amine soluble in hydrocarbons boiling in the
12 gasoline or diesel fuel range.
13
14 37. The fuel composition according to Claim 36, wherein one
15 of R₁ and R₂ is hydrogen or lower alkyl of 1 to
16 4 carbon atoms, and the other is hydrogen.
17
18 38. The fuel composition according to Claim 37, wherein R₂
19 is hydrogen, methyl or ethyl, and R₁ is hydrogen.
20
21 39. The fuel composition according to Claim 36, wherein R
22 is a polyalkyl group having an average molecular weight
23 in the range of about 700 to 3,000.
24
25 40. The fuel composition according to Claim 36, wherein R
26 is a polyalkyl group derived from polypropylene,
27 polybutene, or a polyalphaolefin oligomer of 1-octene
28 or 1-decene.
29
30 41. The fuel composition according to Claim 40, wherein R
31 is a polyalkyl group derived from polyisobutene.
32
33 42. The fuel composition according to Claim 36, wherein A
34 is amino, N-alkyl amino or a polyamine moiety.

- 01 43. The fuel composition according to Claim 42, wherein A
02 is amino.
- 03 44. The fuel composition according to Claim 42, wherein A
04 is a polyamine moiety derived from a polyalkylene
05 polyamine containing from about 2 to about 12 amine
06 nitrogen polyamine atoms and from about 2 to about
07 24 carbon atoms.
- 08
- 09 45. The fuel composition according to Claim 44, wherein the
10 polyalkylene polyamine has the formula:
- 11
- 12
- 13 $\text{H}_2\text{N}- (\text{R}_3-\text{NH})_z-\text{H}$
- 14
- 15 wherein R_3 is an alkylene group having from about 2 to
16 about 6 carbon atoms and z is an integer from about 1
17 to about 4.
- 18
- 19 46. The fuel composition according to Claim 45, wherein the
20 polyalkylene polyamine is ethylene diamine or
21 diethylene triamine.
- 22
- 23 47. The fuel composition according to Claim 36, wherein R
24 is a polyalkyl group derived from polyisobutene, R_1 and
25 R_2 are hydrogen and A is amino or a polyamine moiety
26 derived from ethylene diamine.
- 27
- 28 48. The fuel composition according to Claim 36, wherein
29 said poly(oxyalkylene) amine is a hydrocarbyl
30 poly(oxyalkylene) aminocarbamate.
- 31
- 32 49. The fuel composition according to Claim 48, wherein the
33 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)
34 aminocarbamate contains from 1 to about 30 carbon
atoms; and wherein the amine moiety of said hydrocarbyl

- 01 poly(oxyalkylene) aminocarbamate is derived from a
02 polyamine having from 2 to 12 amine nitrogen atoms and
03 from 2 to 40 carbon atoms.
- 04 50. The fuel composition according to Claim 49, wherein
05 said hydrocarbyl group of said hydrocarbyl
06 poly(oxyalkylene) aminocarbamate is an alkylphenyl
07 group; and wherein said polyalkylene polyamine is
08 selected from the group consisting of ethylenediamine,
09 propylenediamine, diethylenetriamine and
10 dipropylenetriamine.
- 12 51. The fuel composition according to Claim 50, wherein the
13 alkyl moiety of said alkylphenyl group is
14 tetrapropenyl.
- 16 52. The fuel composition according to Claim 48, wherein
17 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an
18 alkylphenyl poly(oxybutylene) aminocarbamate, wherein
19 the amine moiety is derived from ethylenediamine or
20 diethylenetriamine.
- 21 53. The fuel composition according to Claim 36, wherein
22 said poly(oxyalkylene) amine is a hydrocarbyl
23 poly(oxyalkylene) monoamine.
- 25 54. The fuel composition according to Claim 53, wherein
26 said hydrocarbyl poly(oxyalkylene) monoamine is an
27 alkylphenyl poly(oxyalkylene) monoamine, wherein the
28 poly(oxyalkylene) moiety contains oxypropylene units or
29 oxybutylene units or mixtures thereof.
- 31 55. The fuel composition according to Claim 54, wherein the
32 alkylphenyl group is tetrapropenylphenyl.

01

02 56. The fuel composition according to Claim 36, wherein the
03 composition contains from about 25 to about 2,000 parts
04 per million by weight of said
05 polyalkylphenoxyaminoalkane compound and about 25 to
06 about 2,000 parts per million of said poly(oxyalkylene)
07 amine.
08

09 57. The fuel composition according to Claim 36, where the
10 composition further contains from about 25 to about
11 5,000 parts per million by weight of a fuel-soluble,
12 nonvolatile carrier fluid.
13

14 58. A fuel concentrate comprising an inert stable
15 oleophilic organic solvent boiling in the range of from
16 about 150°F. to 400°F. and from about 10 to about
17 70 weight percent of a fuel additive composition
18 comprising:

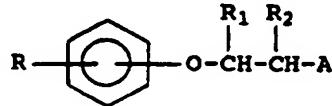
19

20 (a) a polyalkylphenoxyaminoalkane compound of the
21 formula:

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29 or a fuel-soluble salt thereof, wherein R is a
30 polyalkyl group having an average molecular weight
31 in the range of about 600 to 5,000;

32

33 R₁ and R₂ are independently hydrogen or lower
34 alkyl having 1 to 6 carbon atoms; and

- 01 A is amino, N-alkyl amino having about 1 to about
02 20 carbon atoms in the alkyl group, N,N-dialkyl
03 amino having about 1 to about 20 carbon atoms in
04 each alkyl group, or a polyamine moiety having
05 about 2 to about 12 amine nitrogen atoms and about
06 2 to about 40 carbon atoms; and
07
- 08 (b) a poly(oxyalkylene) amine having at least one
09 basic nitrogen atom and a sufficient number of
10 oxyalkylene units to render the poly(oxyalkylene)
11 amine soluble in hydrocarbons boiling in the
12 gasoline or diesel fuel range.
- 13 59. The fuel concentrate according to Claim 58, wherein one
14 of R₁ and R₂ is hydrogen or lower alkyl of 1 to
15 4 carbon atoms, and the other is hydrogen.
- 16 60. The fuel concentrate according to Claim 59, wherein R₂
17 is hydrogen, methyl or ethyl, and R₁ is hydrogen.
- 18 61. The fuel concentrate according to Claim 58, wherein R
19 is a polyalkyl group having an average molecular weight
20 in the range of about 700 to 3,000.
- 21 62. The fuel concentrate according to Claim 58, wherein R
22 is a polyalkyl group derived from polypropylene,
23 polybutene, or a polyalphaolefin oligomer of 1-octene
24 or 1-decene.
- 25 63. The fuel concentrate according to Claim 62, wherein R
26 is a polyalkyl group derived from polyisobutene.
- 27
- 28 64. The fuel concentrate according to Claim 58, wherein A
29 is amino, N-alkyl amino or a polyamine moiety.
- 30
- 31
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-62-

- 01 65. The fuel concentrate according to Claim 64, wherein A
02 is amino.
- 03 66. The fuel concentrate according to Claim 64, wherein A
04 is a polyamine moiety derived from a polyalkylene
05 polyamine containing from about 2 to about 12 amine
06 nitrogen polyamine atoms and from about 2 to about
07 24 carbon atoms.
- 08
- 09 67. The fuel concentrate according to Claim 66, wherein the
10 polyalkylene polyamine has the formula:
11
- 12
- 13 $H_2N-(R_3-NH)_z-H$
- 14
- 15 wherein R_3 is an alkylene group having from about 2 to
16 about 6 carbon atoms and z is an integer from about 1
17 to about 4.
- 18
- 19 68. The fuel concentrate according to Claim 67, wherein the
20 polyalkylene polyamine is ethylene diamine or
21 diethylene triamine.
- 22
- 23 69. The fuel concentrate according to Claim 58, wherein R
24 is a polyalkyl group derived from polyisobutene, R_1 and
25 R_2 are hydrogen and A is amino or a polyamine moiety
26 derived from ethylene diamine.
- 27
- 28 70. The fuel concentrate according to Claim 58, wherein the
29 fuel concentrate further contains from about 20 to
30 about 60 weight percent of a fuel-soluble, nonvolatile
31 carrier fluid.
- 32
- 33 71. The fuel concentrate according to Claim 58, wherein
34 said poly(oxyalkylene) amine is a hydrocarbyl
poly(oxyalkylene) aminocarbamate.

- 01 72. The fuel concentrate according to Claim 71, wherein the
02 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)
03 aminocarbamate contains from 1 to about 30 carbon
04 atoms; and wherein the amine moiety of said hydrocarbyl
05 poly(oxyalkylene) aminocarbamate is derived from a
06 polyamine having from 2 to 12 amine nitrogen atoms and
07 from 2 to 40 carbon atoms.
- 08 73. The fuel concentrate according to Claim 72, wherein
09 said hydrocarbyl group of said hydrocarbyl
10 poly(oxyalkylene) aminocarbamate is an alkylphenyl
11 group; and wherein said polyalkylene polyamine is
12 selected from the group consisting of ethylenediamine,
13 propylenediamine, diethylenetriamine and
14 dipropylenetriamine.
- 16 74. The fuel concentrate according to Claim 73, wherein the
17 alkyl moiety of said alkylphenyl group is
18 tetrapropenyl.
- 20 75. The fuel concentrate according to Claim 71, wherein the
21 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an
22 alkylphenyl poly(oxybutylene) aminocarbamate, wherein
23 the amine moiety is derived from ethylenediamine or
24 diethylenetriamine.
- 26 76. The fuel concentrate according to Claim 58, wherein
27 said poly(oxyalkylene) amine is a hydrocarbyl
28 poly(oxyalkylene) monoamine.
- 29 77. The fuel concentrate according to Claim 76, wherein
30 said hydrocarbyl poly(oxyalkylene) monoamine is an
31 alkylphenyl poly(oxyalkylene) monoamine, wherein the
32 poly(oxyalkylene) moiety contains oxypropylene units or
33 oxybutylene units or mixtures thereof.

-64-

01 78. The fuel concentrate according to Claim 77, wherein the
02 alkylphenyl group is tetrapropenylphenyl.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07915

A. CLASSIFICATION OF SUBJECT MATTER		
IPC(6) : C10L 1/22 US CL : 044/424, 425, 432, 433, 434 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) U.S. : 044/424, 425, 432, 433, 434		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched none		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS search terms: polyoxyalkylene amine, fuel, ?phenoxyaminoalkane		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,366,517 A (CHERPECK) 22 November 1994, col. 2, lines 20-54.	1, 21-36, 48-58, 71-78
A	US 5,300,701 A (CHERPECK) 05 April 1994, col. 2, lines 10-33.	1-78
Y	US 5,094,667 A (SCHILOWITZ et al) 10 March 1992, col. 1, lines 32-61.	1, 21, 22, 33, 36, 53, 58, 76
Y	US 4,964,879 A (HERBSTMAN et al) 23 October 1990, col. 2, lines 3-31.	1, 21, 22, 33, 36, 53, 58, 76
Y	US 4,778,481 A (COURTNEY) 18 October 1988, col. 2, lines 7-51.	1, 21-32, 36, 48-52, 58, 71-75
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <ul style="list-style-type: none"> *A* document defining the general state of the art which is not considered to be of particular relevance *T* earlier document published on or after the international filing date *U* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another claim or other special reasons (as specified) *W* document referring to an oral disclosure, use, exhibition or other source *P* document published prior to the international filing date but later than the priority date claimed 		<p>T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>TX document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>TY document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>WP document member of the same patent family</p>
Date of the actual completion of the international search	Date of mailing of the international search report	
27 JUNE 1997	24 JUL 1997	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer <i>Angela Walker</i> ELLEN M. MCAVOY Telephone No. (703) 308-0661	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07915

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,609,377 A (SUNG et al) 02 September 1986, col.1, lines 28-44.	1, 21, 22, 33-36, 53-55, 58, 76-78
A	US 4,604,103 A (CAMPBELL) 05 August 1986, col. 5, lines 31-51.	1-78
A	US 4,332,595 A (HERBSTMAN et al) 01 June 1982, col. 1, lines 63 to col. 2, line 9.	1-78
A	US 4,322,220 A (MACHLEDER et al) 30 March 1982, col. 2, lines 20-34 and col. 17, lines 55-65.	1-78
A	US 4,024,083 A (KABLAOUI et al) 17 May 1977, col. 1, lines 52-63.	1-78
A	US 3,440,029 A (LITTLE et al) 22 April 1969, col. 1, lines 16-26.	1-78